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Air Force Research Laboratory

Hydrolytic Network Structure Degradation in Multi-Component Polycyanurate Networks

28 July 2016

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Integrity ★ Service ★ Excellence

Outline

- Background
- Quantitative Models
- New Data

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- Mr. Michael Ford, chemistry support

Cyanate Esters for Next-Generation Aerospace Systems

Glass Transition Temperature
200 – 400 °C (dry)
150 – 300 °C (wet)

Onset of Weight Loss:
> 400 °C with High Char Yield

Resin Viscosity Suitable for Filament Winding / RTM

Good Flame, Smoke, & Toxicity Characteristics

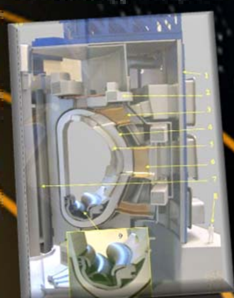
Compatible with Thermoplastic Tougheners and Nanoscale Reinforcements

Low Water Uptake with Near Zero Coefficient of Hygroscopic Expansion

Cyanate Esters Around the Solar System

Our Solar System

- On Earth, cyanate ester / epoxy blends have been qualified for use in the toroidal field magnet casings for the ITER thermonuclear fusion reactor



Fusion reactor, photo courtesy of Gerritse ((Wikimedia Commons)

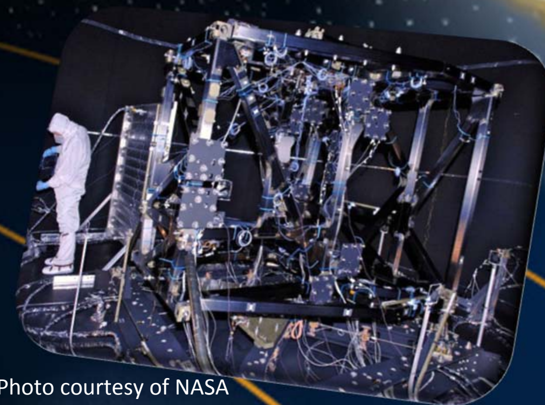


Photo courtesy of NASA

- Unique cyanate ester composites have been designed by NASA for use as instrument holding structures aboard the James Webb Space Telescope

- The science decks on the Mars Phoenix lander are made from M55J/cyanate ester composites

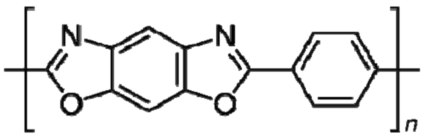
- The solar panel supports on the MESSENGER space probe use cyanate ester composite tie layers

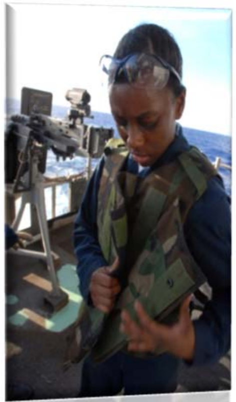
Images: courtesy NASA (public release)

Importance of Moisture Uptake in Composite Component Performance

Photo by U.S. Navy photo by Photographer's Mate 1st Class Anibal Rivera (public domain).

U.S. Navy photo by Photographer's Mate 3rd Class Mark J. Rebilas (RELEASED)



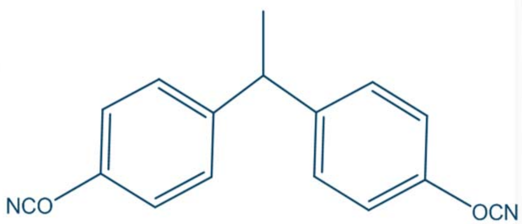


U.S. Navy photo by Mass Communication Specialist 3rd Class Torrey W. Lee (public domain)

- Water can add significantly to launch or take-off weight (3% water in composite resins = about 50 lbs of extra weight on an large SRM)
- Items with high water content can fail catastrophically when suddenly heated
- Long-term exposure to water can facilitate many mechanisms of chemical degradation, necessitating substantial "knock down" factors in design allowables
- Though more stable than epoxy resins, cyanate esters can degrade on long-term exposure to hot water

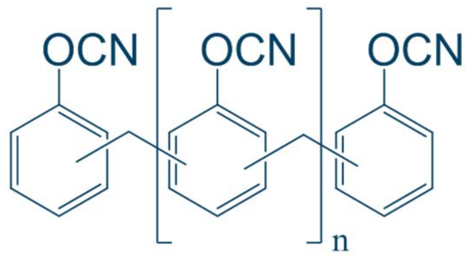
Materials Utilized

Monomers



LECy

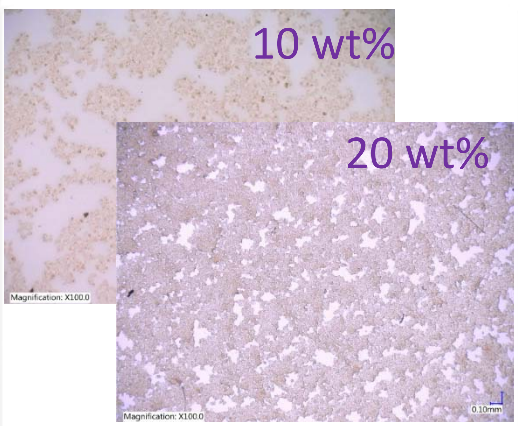
Mixture



PT-30

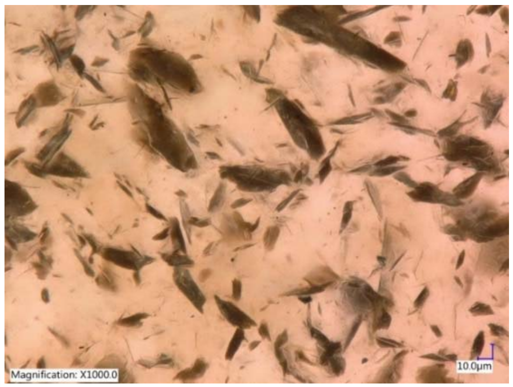
LECy/PT-30 (50/50 by weight) co-cured networks were cured at 170, 190, 210, and 240 C for 8 hrs to achieve a variety of conversion. Catalyst used was 160 ppm Cu as Cu-acac with 2 phr nonylphenol.

Additives



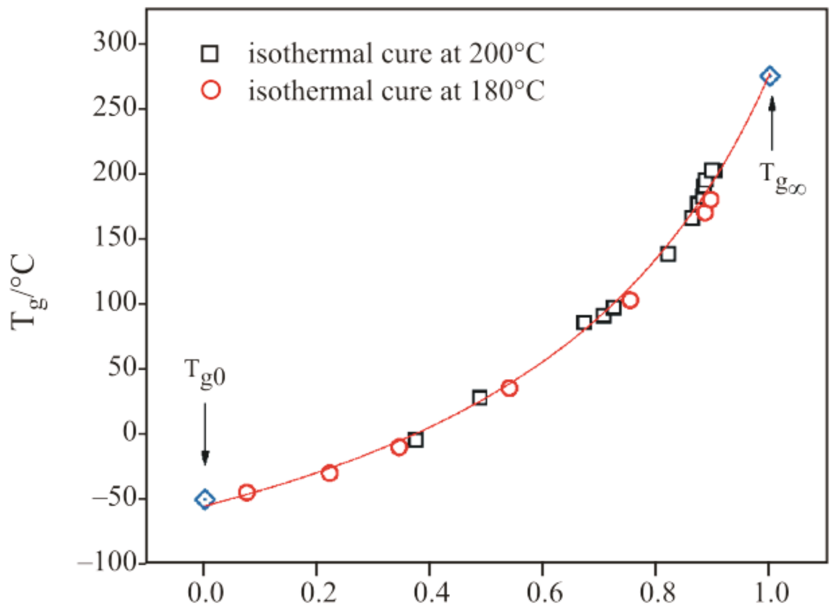
PEEK, 15 wt%

4-K Mica, 10 wt%



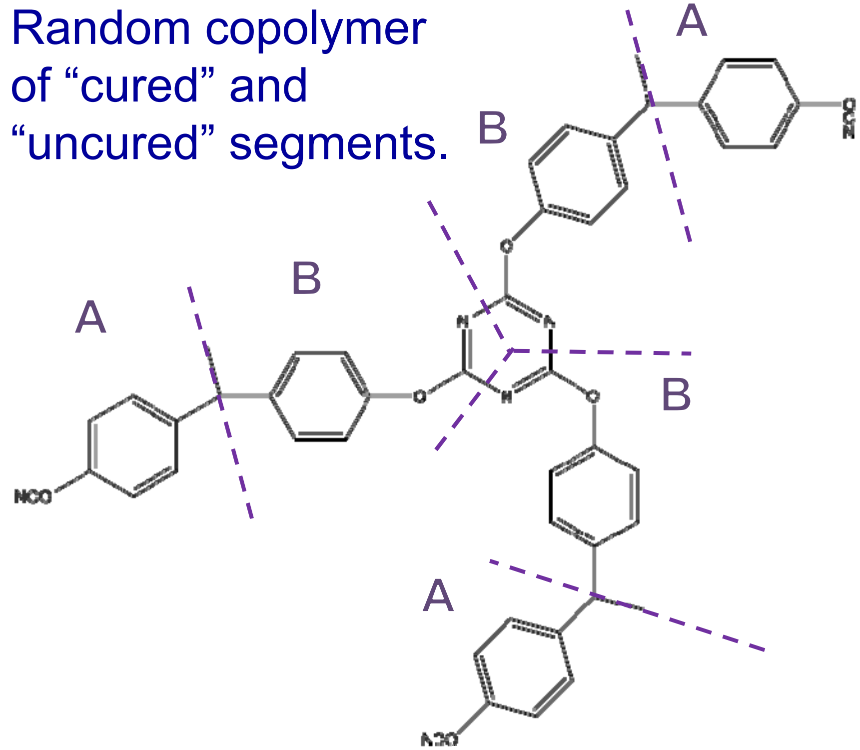
Suzorite 325-S Mica, 10 wt%

Models for Network Initial States



from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, *93*, 77-85 for EX-1510

Random copolymer of "cured" and "uncured" segments.



DiBenedetto equation is just Gordon-Taylor equation recast with 1-α = ϕ_1, λ = k

No volume change on cure, so α = ϕ_{cured}

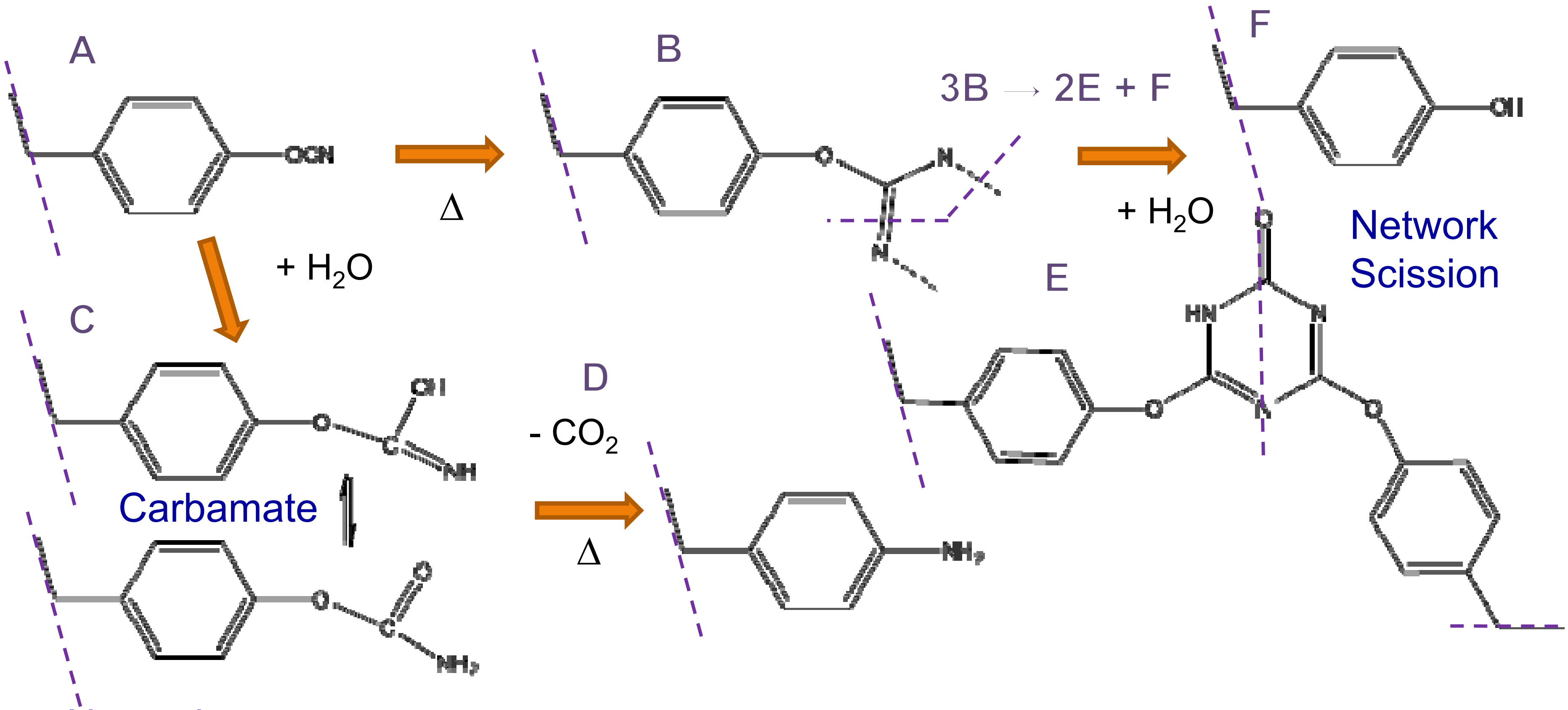
<u>Assumptions:</u>

ΔH_{mix} = 0; ΔS_{mix} = 0, Δv_{mix} = 0,
S continuous at T_G, $dS//dP$ = 0

<u>Consequence</u>

Initial state of network entirely described by one parameter - α

Chemical Reaction Scheme



Network states:

ϕ_A, … ϕ_F ϕ_E and ϕ_F related by stoichiometry

If networks are heated only to 350 °C, then only one of ϕ_C or ϕ_D may be non-zero.

Result: three parameters prior to heating: network conversion α' based on ϕ_B ,plus ϕ_C and ϕ_F. Two parameters after heating, ϕ_D and ϕ_F.

Chemical Reaction Models

Carbamate formation

$A \rightarrow C$

Weight gain of $0.14\phi_c$

Loss of ΔH_{cure}, Loss of FT-IR signal at 2250 cm^{-1}, gain in FT-IR signal at 1700 cm^{-1}, no change in T_G

Residual Cure

$A \rightarrow B$

Heating to 350 °C dry will complete

No weight change

Loss of ΔH_{cure}, Loss of FT-IR signal at 2250 cm^{-1}, increase in T_G

Carbamate decomposition

$C \rightarrow D$

Heating to 350 °C will complete

Weight loss of $0.34\phi_c$

No change in ΔH_{cure}, Loss of FT-IR signal at 17000 cm^{-1}, no change in T_G

Network Scission

$3B \rightarrow 2E + F$

Weight gain of $0.14\phi_E$

No change in ΔH_{cure}, only discernible readily via near-IR, decrease in T_G

Other decomposition

$E \rightarrow G$, $B \rightarrow H,A$, $A \rightarrow I$

Assumed negligible below 350 °C

More details:

Davis, M. C.; Guenthner, A. J.; Sahagun, C. M.; Lamison, K. R.; Reams, J. T.; Mabry, J. M. "*Polymer* **2013**, *54*, 6902-6909.

Marella, V. V.; Throckmorton, J. A.; Palmese, G. R. *Polym. Degrad. Stabil.* **2014**, *104*, 104-111.

Effective Conversion Reduction

Multi-Component Gordon-Taylor Equation:

$T_G = (T_{GA}\,\phi_A + k_{BA}\,T_{GB}\,\phi_B + \ldots + k_{EA}\,T_{GF}\,\phi_F) / (\phi_A + k_{BA}\,\phi_B + \ldots + k_{FA}\,\phi_F)$

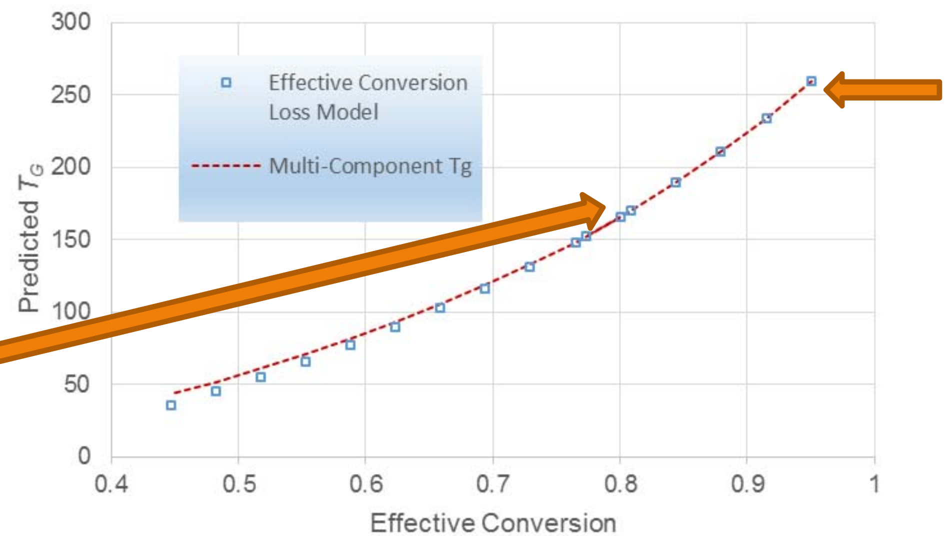
Can be simplified using an "effective conversion reduction factor" *K*

$\alpha'_{eff} = \alpha'_0 - K\phi_F$

$T_G = T_{G0} + (T_{G\infty} - T_{G0})\,\lambda\,\alpha'_{eff} \;/\; [1 - (1-\lambda)\,\alpha'_{eff}]$ *(just the diBenedetto equation)*

Assumes: Same network physics throughout hydrolysis; ϕ_C and ϕ_F are correlated

Test 1: Use K from $\phi_F = 0.02$; (Test 1) extrapolate to $\phi_F = 0.2$ with $\alpha'_0 = 0.8$ and $\phi_C / \phi_F = 1$; Max error 8 °C

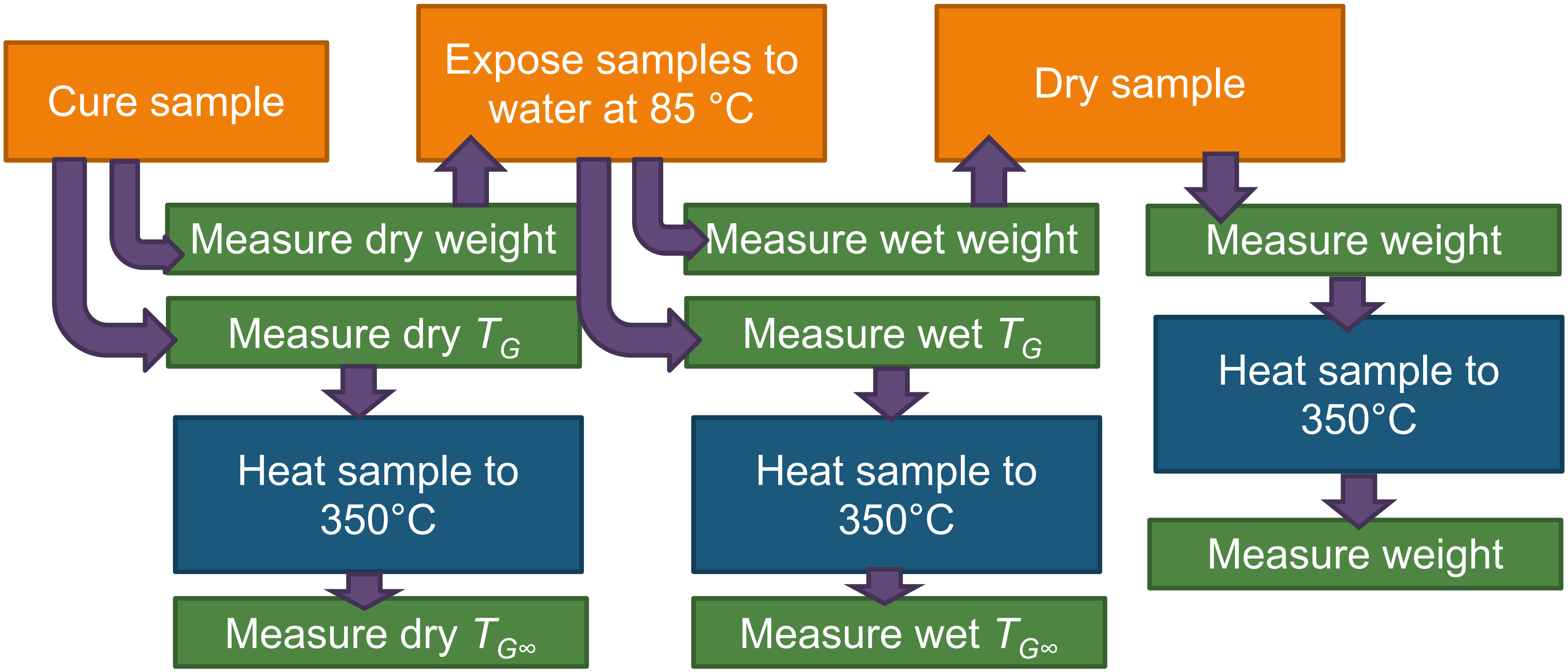


Test 1: Use K from $\phi_F = 0.02$; $\alpha'_0 = 0.95$, $\phi_C / \phi_F = 0.5$; extrapolate to $\phi_F = 0.1$. Max error 1 °C

Test Parameters; $k_{BA} = 0.4$; $T_{GB} = 300$ °C; $k_{CA} = 1.2$; $T_{GC} = 0$ °C; $k_{DA} = 0.9$; $T_{GD} = -30$ °C; $k_{EA} = 0.6$; $T_{GE} = 100$ °C; $k_{FA} = 0.8$; $T_{GF} = -20$ °C;

Analysis Procedure

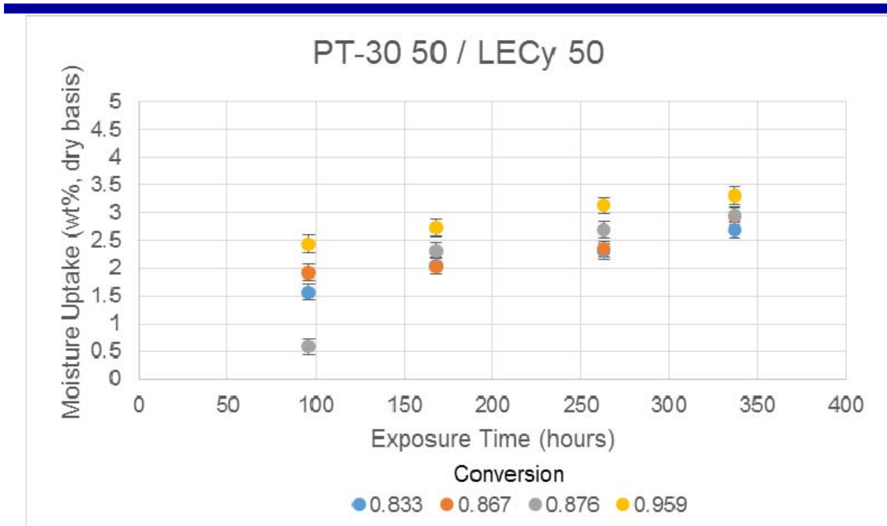
Assumes diBenedetto parameters are known

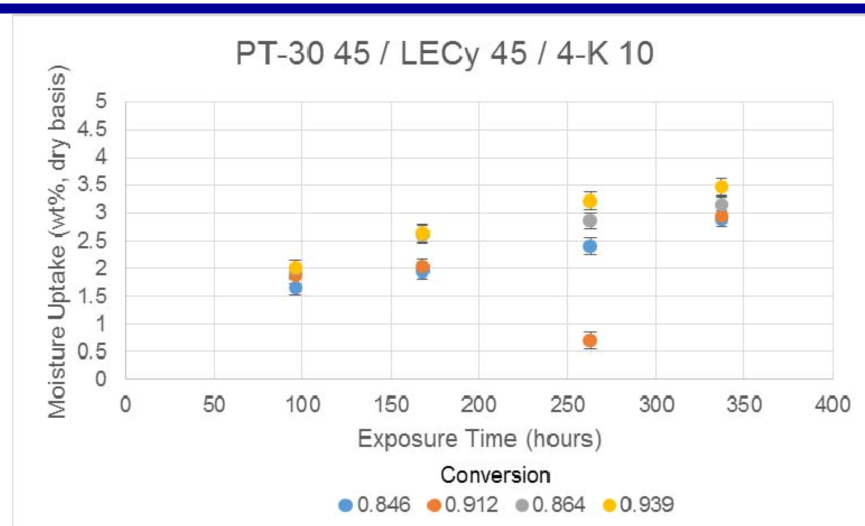


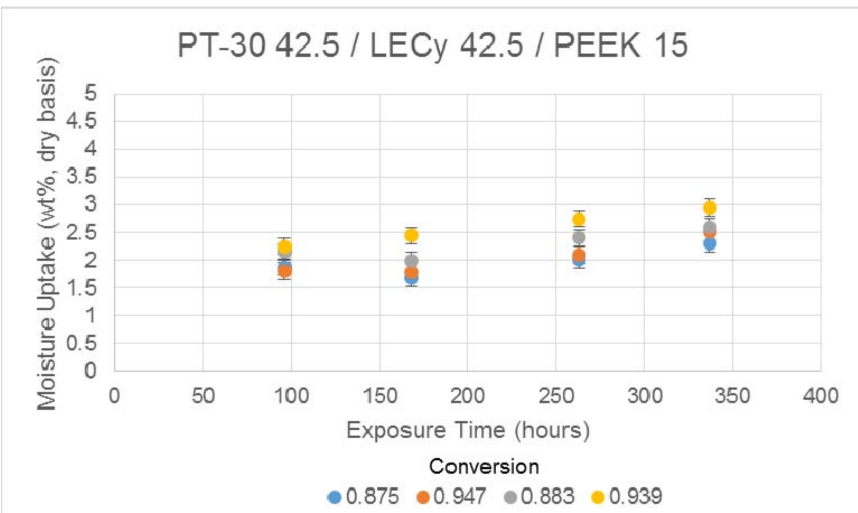
FT-IR may be added for verification if possible. Dry sample glass transition best if measured by DSC; wet glass transition best if measured by TMA

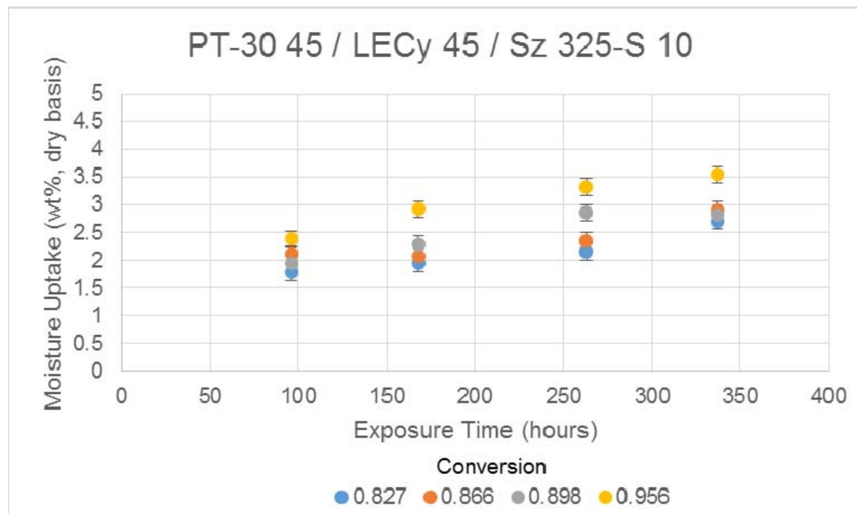
Final "wet and dried" weights determine – ϕ_C, ϕ_F. $T_{G\infty}$ data cross-checks other degradation.

Weight Gain After Water Exposure (No Drying)



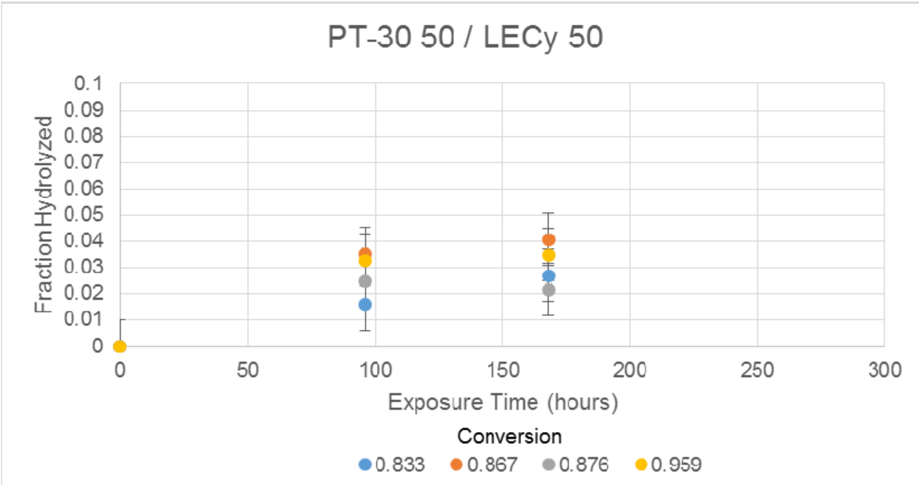


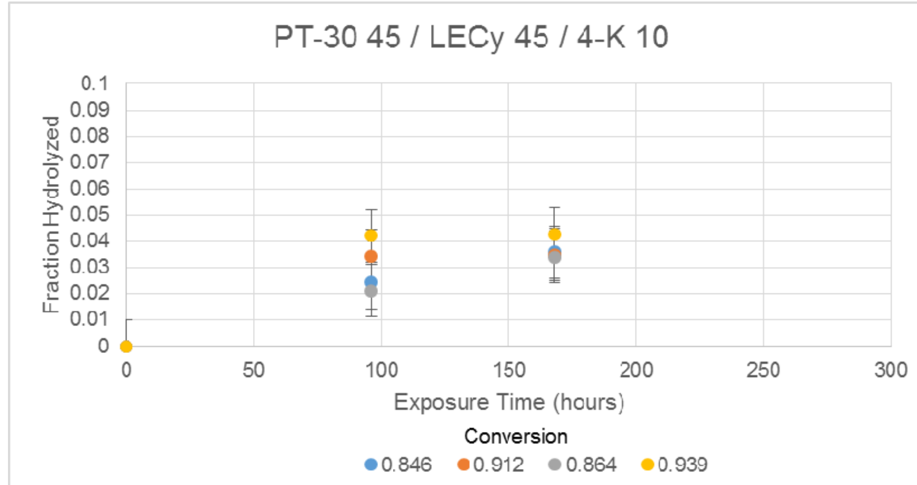


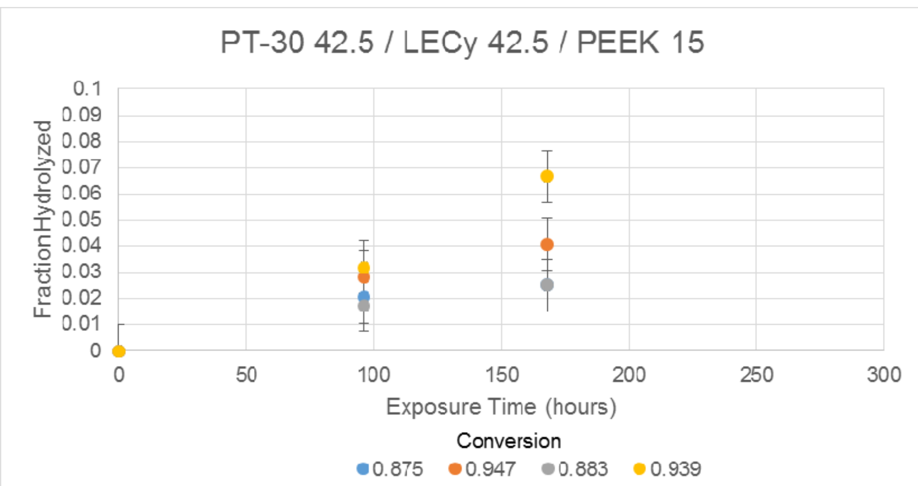


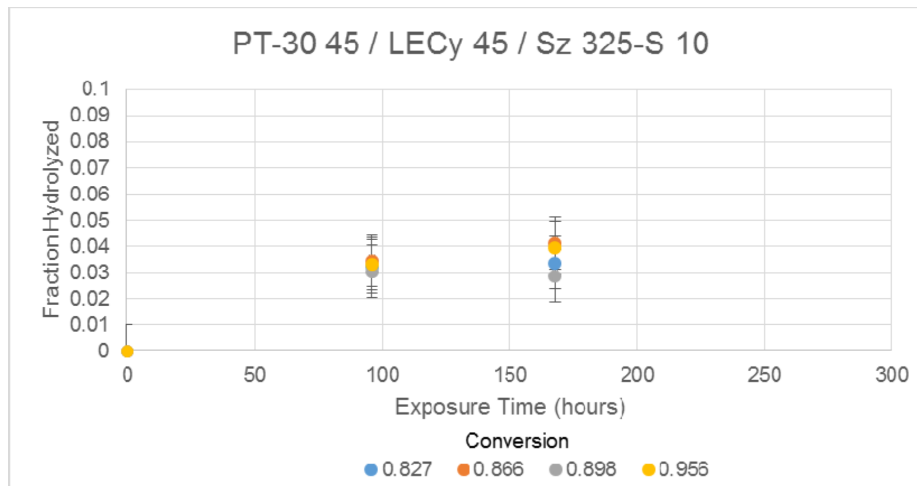
Slow hydrolysis evident; conversion dependence as expected
PEEK reduces water uptake as expected

Hydrolysis Extent After Water Exposure



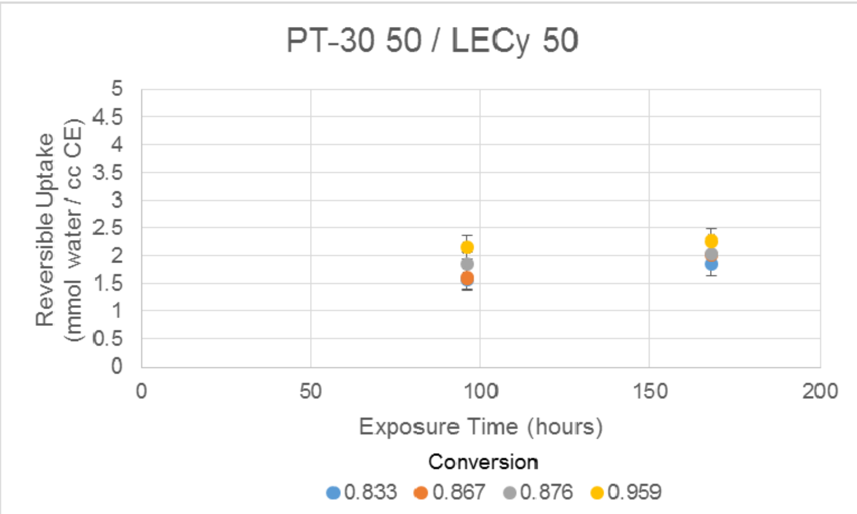


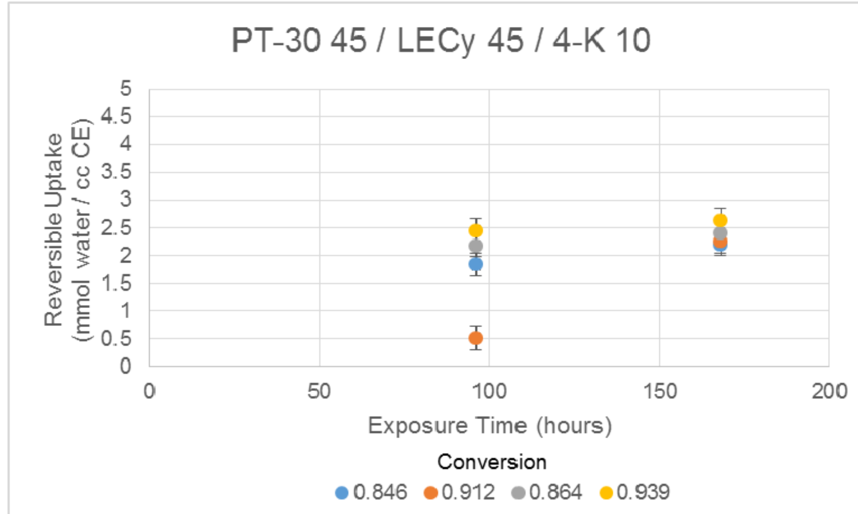


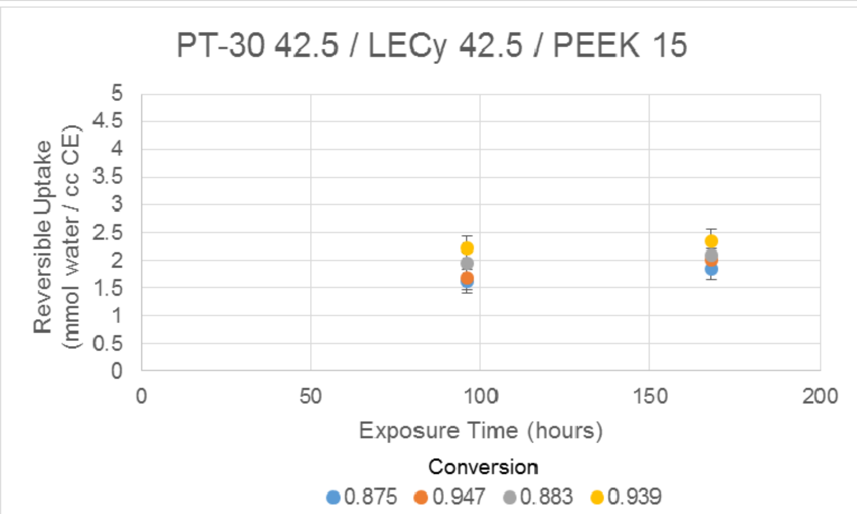


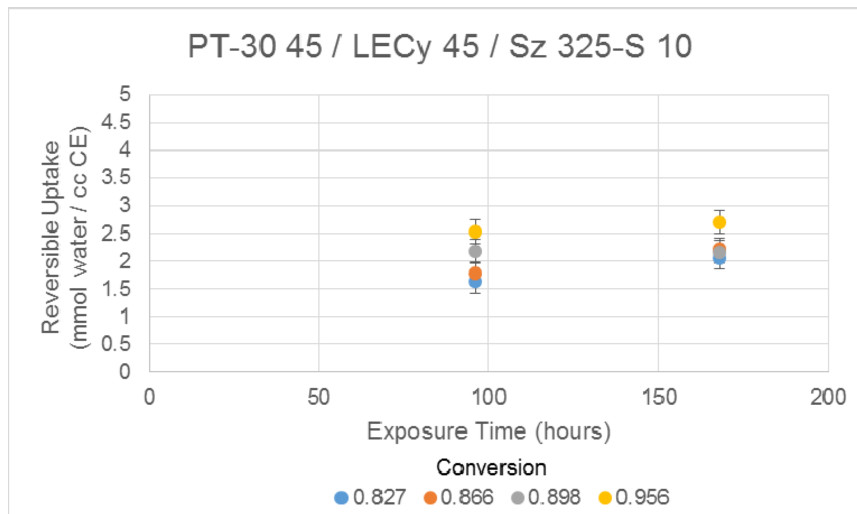
Data from samples exposed and dried with mild heating; slight correlation with conversion; additives show little effect so far …

Estimated Water Concentration



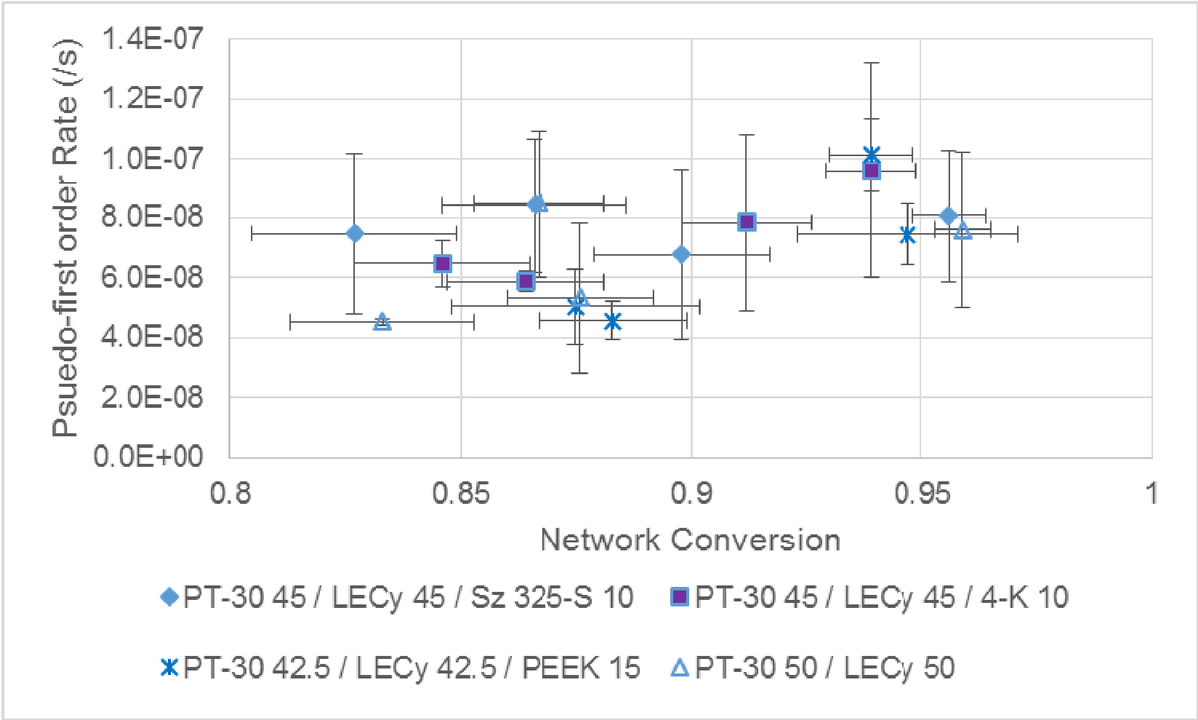






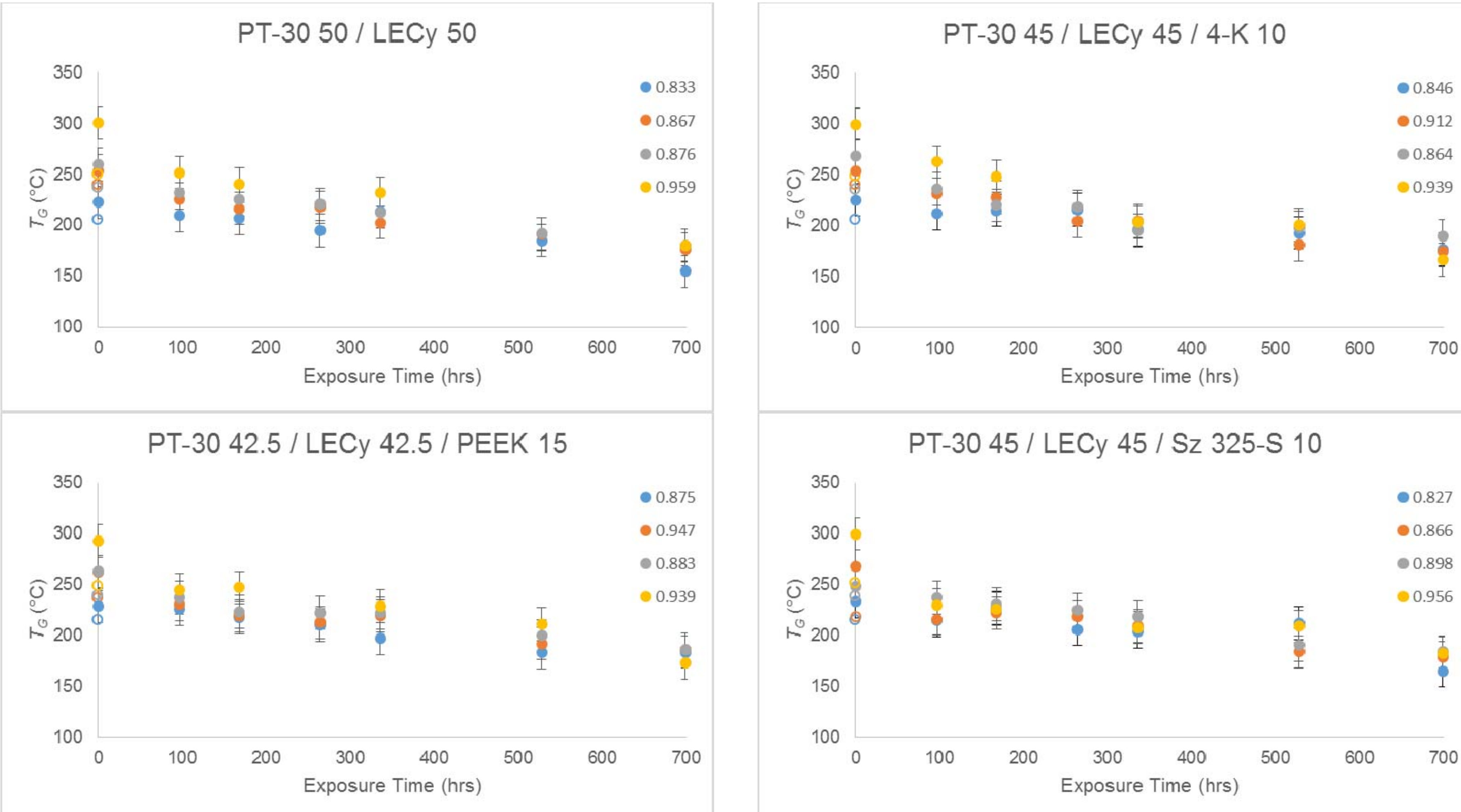
Mica appears to add water and inhibit diffusion. Diffusion appears to be faster at higher conversions.

Preliminary Kinetic Data



Conversions are from DSC only and are preliminary
Rate constant is for all hydrolysis reactions – includes carbamate formation and network scission

Glass Transition Temperature



DSC data for dry samples is shown as open symbols; in-situ cure affects results at early times, even after exposure, proving –OCN groups are still present

Summary

- The relative simplicity of the chemical structure of polycyanurate networks, in combination with ease of analysis, allows for quantitative modeling of hydrolytic degradation. These models link chemical structure, physical properties, and environmental conditions, while allowing for validation.
- Hydrolytic degradation processes have been quantified for Cu/nonylphenol-catalyzed, co-cured LECy/PT-30 networks, with and without additives for toughening, under exposure to hot water. The effects of conversion have been examined.
- Preliminary data shows rates of hydrolysis that are lower than for PT-30 alone. Overall hydrolysis rates appear to be slightly higher at higher conversions, suggesting that carbamate formation is not responsible for a large portion of weight gain.
- Glass transition temperatures decrease gradually as expected. Determination of the effective network conversion reduction parameter requires further work to distinguish carbamate formation from network scission.